The dislocation-free growth of gadolinium gallium garnet single crystals

B. COCKAYNE, J. M. ROSLINGTON
Royal Radar Establishment, Malvern, Worcestershire, UK

It is established that a substantial number of the microscopic strain centres observed in Czochralski-grown gadolinium gallium garnet single crystals are due to dislocations whose propagation is markedly dependent upon the shape of the solid/liquid interface. It is shown that the dislocation density can be minimized by using facets to block dislocation propagation and that crystals substantially free from dislocations can be produced.

1. Introduction

Gadolinium gallium garnet ($Gd_3Ga_5O_{12}$ or GGG) single crystals are now widely employed as substrates for both liquid-phase epitaxial deposition and chemical vapour deposition of magnetic garnet thin films used in bubble-domain devices. The structural perfection of the substrate plays an important role in determining the quality of the thin film produced and a number of defects such as iridium particles, precipitates of Gd_2O_3 and Ga_2O_3 and strained faceted regions have already been identified [1-3]. In this paper, the nature and control of linear defects are examined.

2. Experimental details

The GGG crystals studied were grown by the Czochralski technique using the apparatus described earlier for the growth of sapphire [4]. The melts were prepared from stoichiometric mixtures of the component oxides, Ga_2O_3 and Gd_2O_3, which were supplied respectively by Johnson Matthey Chemicals Ltd and Rare Earth Products Ltd as crystal-growing grade materials. The crystals were grown from a 3.8 cm diameter × 3.3 cm deep iridium crucible using a gas ambient of nitrogen/10 vol % oxygen with a total flow rate of 350 cc min^{-1}. A pull rate of 7 mm h^{-1} and rotation rates within the range 10 to 100 rev min^{-1} were used. The crystal orientation used as the growth direction was <111> in all cases. Crystal sections for optical microscopy were prepared using standard cutting and polishing techniques. For the etching experiments, the work damage induced by the preparative techniques was removed by chemical polishing in an orthophosphoric acid bath for approximately 10 min at a temperature of 280°C The specimens for X-ray topography were thinned in the same manner to 50 to 100 μm and examined using Ag$K\alpha$ radiation. Dislocation etch pits were revealed using either molten PbO containing a trace of GGG at a temperature of 900°C [5] or orthophosphoric acid at a temperature of 300°C. The former etching technique works on all mechanically-polished surfaces whilst the latter requires syton-polished surfaces to prove most effective.

3. Results

Single crystals of many garnet crystals grown from the melt, develop a solid/liquid interface which is convex towards the melt and upon which facets of the type {211} and {110} readily form [6, 7]. These facets produce a macroscopic strain pattern which is normally symmetrically displaced about the growth axis. A macroscopic strain pattern of this type in a <111> -axis GGG crystal is shown in Fig. 1a. Interfaces sufficiently convex to develop facets occur at low crystal-rotation rates, typically 10 to 50 rev min^{-1}, the particular rate required to produce a given interface shape, being dependent upon the ratio of crystal diameter/crucible diameter and the degree of insulation/afterheating used. At higher crystal-rotation rates, typically 80 to 100 rev min^{-1}, the interface becomes planar or concave, facets no longer form, and the macroscopic strain effect is eliminated (Fig. 1b). However, transverse sections of crystals grown under facet-free condi-

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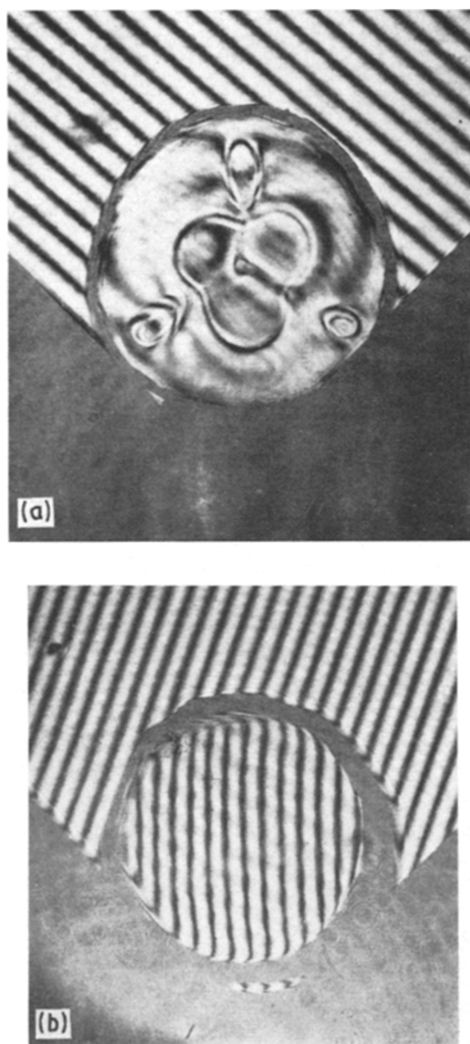


Figure 1 Interferometric strain pattern through 1 cm crystal lengths grown at a rate of (a) 10 rev min^{-1}, showing 3 × {211} facets at the centre and 3 × {110} facets nearer the circumference (crystal diameter = 1.7 cm), (b) 80 rev min^{-1}, showing an absence of facets (crystal diameter = 1.7 cm).

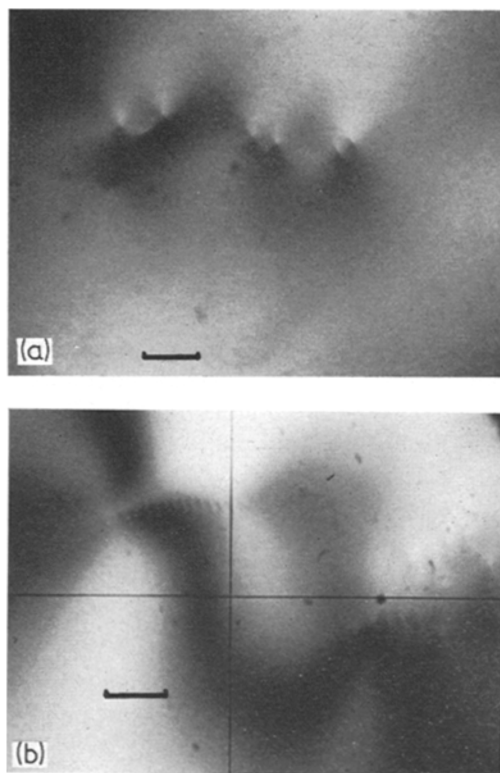


Figure 2 Transverse (111) crystal sections showing (a) strain centres (marker = 200 μm), (b) strain arrays (marker = 100 μm).

tions show microscopic strain features which are evident as strain around particular points or arrays of points (Fig. 2). These points are only visible under crossed polars and do not correspond to any detectable precipitate or iridium particles. By focusing through the transverse section, the points can be seen to correspond to the intersection of needle-like regions of strain with the section surface. These regions approximate to lines which are propagated almost parallel to the growth axis of the crystal, sometimes for distances of several centimetres. The most intense regions of strain are caused by the arrays. In any particular array, the spacing between strain centres is approximately constant but between one array and another the spacing can vary by a factor of 2, typical values lying between 20 and 40 μm. In regions away from the arrays, the strain centres frequently occur in pairs.

The presence of arrays and pairs in conjunction with the absence of any particle at the middle of the strain centres suggests that this particular defect is due to the presence of dislocations with a large strain field. This hypothesis tends to be confirmed by etching studies which reveal both pairs and arrays of pits corresponding directly to the strain centres (Fig. 3). X-ray topographic studies of thin sections of crystals containing these defects substantiates the view that the arrays and points correspond to dislocations. A topo-

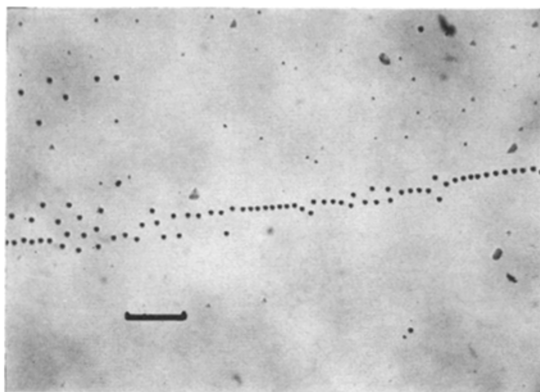


Figure 3 Dislocation etch pits on a (111) transverse crystal section showing arrays and pairs; some triangular and irregular shaped iridium particles can also be seen (marker = 200μm).

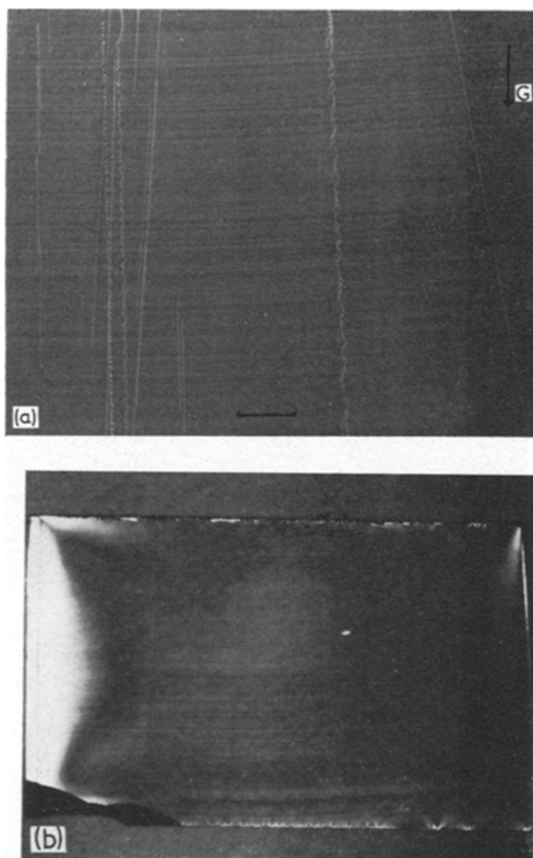


Figure 4 (a) X-ray topograph of a (110) longitudinal crystal section showing linear and helical dislocations in addition to growth striations, G indicates growth direction (marker = 1 mm). (b) The same crystal section viewed optically showing lines of strain and growth striations (crystal diameter = 1.8 cm).

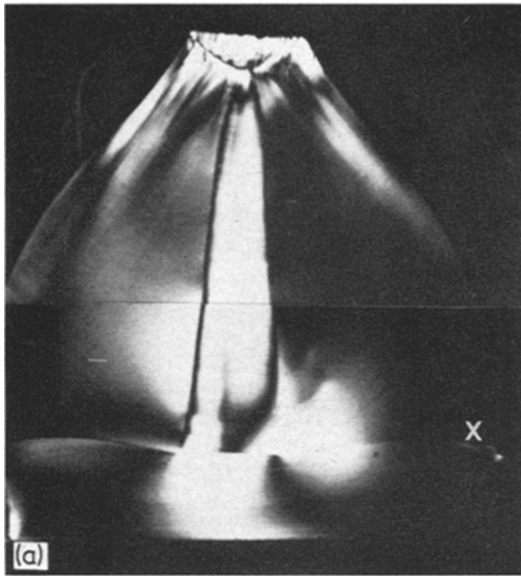
graph of a longitudinal section of crystal (Fig. 4a) shows linear and helical features characteristic of dislocation structures which can be directly equated to the line features observed optically in the same sample prior to thinning (Fig. 4b).

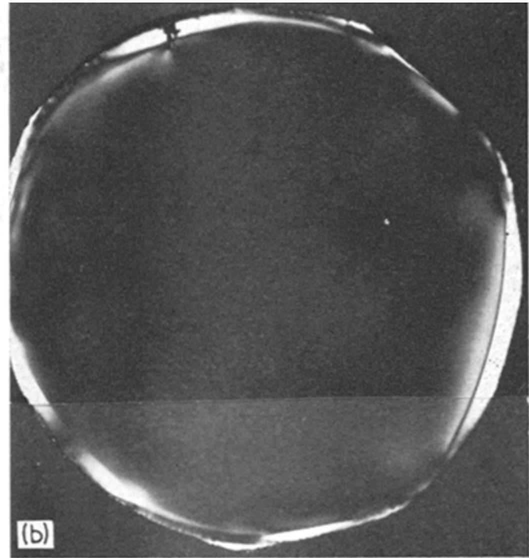
The differences in dislocation density in faceted and non-faceted crystals is very marked. Examination of some forty crystals has shown that all the crystals containing facets are dislocation-free whilst those which are facet-free usually contain dislocations. Counts of strain centres and etch pits show that the dislocation density in facet-free crystals is typically 50 to 500 cm^{-2}. The extensive distances for which the dislocations are propagated, permits the source of many of the dislocations to be traced. With few exceptions, they appear to be generated from the seed/crystal interface.

The presence of facets in the region just below the seed/crystal junction produces two main effects. Firstly, the facets block dislocation propagation over the volume of crystal they occupy and secondly, cause the strain associated with seeding to be propagated towards the crystal edge rather than parallel to the growth axis. Similar radially-propagated strains adjacent to facets have been observed previously in $Y_3Al_5O_{12}$ single crystals [7].

Clearly, facets can be used to restrict dislocation propagation but the facets themselves represent regions of strain and also have to be removed in order to yield structurally-perfect material. Fig. 5a shows how facets can be used to block dislocation propagation in the region below the seeding-on position and that the facets can subsequently be removed by flattening the solid/liquid interface. The faceted region was grown with a crystal-rotation rate of 30 rev min^{-1} but, when the required crystal diameter had been achieved (X), the rotation rate was increased linearly to 80 rev min^{-1} over a period of 1 h in order to produce the facet-free interface. Fig. 5b is a transverse section of a lower part of this crystal showing a complete absence of the strain centres and arrays associated with dislocations. This is in contrast to the crystal section of Fig. 5c which was prepared from a crystal grown entirely with a planar interface.

It is very important to prevent the development of a concave interface during both the





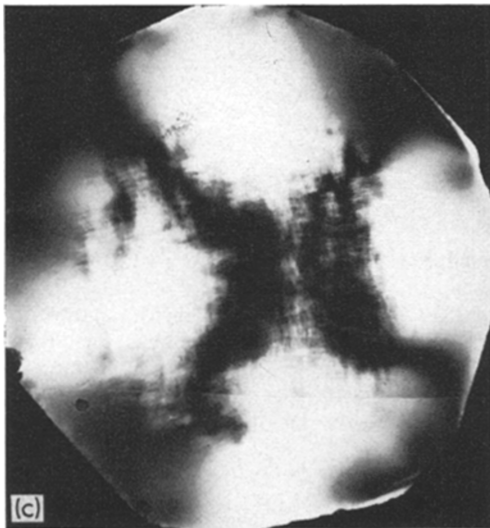


Figure 5 (a) A longitudinal crystal section showing the effect of facets on the strain induced by seeding and interface flattening at X to effect facet removal (crystal diameter = 1.9 cm). (b) A transverse section of a lower part of the crystal in Fig. 5a showing an absence of dislocation strain centres (crystal diameter = 1.9 cm). (c) A transverse section of a crystal grown without using facet development to restrict dislocation propagation showing extensive dislocation strain arrays (crystal diameter = 1.9 cm).

outgrowth to full diameter and the melting-back process which occurs at the facet removal stage because such an interface leads to dislocation generation, presumably due to the strain associated with the enhanced entrapment of segregating components/impurities which occurs with this type of interface. By using facet blocking in conjunction with interface flattening, the dislocation density can be reduced by an order of magnitude to less than 10 cm^{-2} and with ultra-careful control of the crystal-rotation rate during the changes in interface shape, dislocation-free crystals can be obtained.

4. Discussion and conclusions

It is clearly established that the majority of microscopic strain centres observed in $<111>$ axis GGG crystals are dislocations. These can be generated during seeding, which thermally stresses the crystal interface, or by the development of a concave interface, which promotes the entrapment of segregating components. This behaviour is in contrast to yttrium aluminium garnet which is isostructural but, under comparable growth conditions, shows neither of these effects. The major difference between the two materials is that GGG contains a volatile component, namely Ga_2O_3, which can react with the iridium crucible to make precise stoichiometry control difficult [2]. The presence of dislocations in GGG is surprising as the complex cubic garnet lattice, with a large unit cell [8], does not readily lend itself to dislocation formation due to the potentially-large Burgers vectors and high energies involved. Deviations from stoichiometry could account for this behaviour as such changes markedly alter the

resistance of a lattice to deformation. The presence of helices and growth striations suggests that such deviations are possible, as formation mechanisms for both these features [9, 10] require a supersaturation of either component or impurity atoms; an imbalance of component atoms is the most likely possibility because of the complex melt/crucible/gas ambient reactions [2] and the use of high purity starting materials.

The use of facet formation to restrict dislocation propagation is a novel feature in Czochralski growth. The mechanism by which facets block dislocation propagation has not yet been established; differences in composition [3] leading to lattice hardening and differences in nucleating behaviour are both possibilities. The use of facets in this manner, with interface shape changes to effect facet removal at a later stage of growth, has improved the structural perfection of GGG crystals by an order of magnitude and allowed substrate materials free from both localized and macroscopic strain centres to be produced.

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